EFFICIENCY OF MOLECULAR HYDROGEN FORMATION ON SILICATES

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ABSTRACT

We report on laboratory measurements of molecular hydrogen formation and recombination on an olivine slab as a function of surface temperature under conditions relevant to those encountered in the interstellar medium. On the basis of our experimental evidence, we recognize that there are two main regimes of H coverage that are of astrophysical importance; for each of them we provide an expression giving the production rate of molecular hydrogen in interstellar clouds.

Subject headings: dust— ISM; abundances — ISM; molecules — molecular processes

1. Introduction

Recently, we measured (Pirronello et al. 1997) the synthesis of molecular hydrogen for the first time on a surface of a solid of astrophysical interest, a slab of natural olivine (a silicate made of a mixture of (Mg_2SiO_4 and Fe_2SiO_4)), and in experimental conditions close to those encountered in interstellar clouds. The importance of these measurements comes from the relevance of molecular hydrogen in the interstellar medium and from the impossibility to form it at the required rate (Jura 1975) in gas phase reactions in such low density an environment.

This fundamental problem has been addressed by several authors (among them, Gould and Salpeter 1963, Hollenbach and Salpeter 1970 and 1971, Smoluchowski 1981 and 1983, Leitch-Devlin and Williams 1984 and 1985, Duley and Williams 1986, Buch and Zhang 1991) who reached different and sometimes conflicting conclusions. Most of the work up to now is based on the following simple expression of the production rate $R_{H_2}(\mathrm{cm}^{-3}\mathrm{sec}^{-1})$ of molecular hydrogen:

$$R_{H_2} = \frac{1}{2}n_H v_H A n_g S_H \gamma \qquad (1)$$

where S_H the sticking coefficient (i.e., the probability that an atom hitting the surface remains on it), n_H the number density, v_H the speed of H atoms in the gas phase, A the cross-sectional area of the grain, and n_g the number density of dust grains. γ is the probability that two hydrogen atoms on the surface meet and recombine; such a probability is usually taken to be equal or close to one, based on the assumption that, even at interstellar dust temperatures, the mobility of H adatoms by tunneling is so high that they meet and form H_2 before having a chance to evaporate.

The few experimental attempts (Brackmann and Fite 1961, Schutte et al. 1976) were performed in conditions and on samples that were too different from the interstellar

ones to be useful. Therefore, the choice to measure H_2 formation on a natural silicate is justified by the necessity to evaluate the rate on a more realistic surface (Mathis and Whiffen 1989) than the one of a model, even if we know that some difficulties do exist. For example, it has been suggested that silicates might be destroyed by the UV radiation field (Hong and Greenberg, 1980, Greenberg and Li 1996); furthermore, silicates in space are probably amorphous (Draine and Lee 1984) , while specimens on Earth are polycrystalline, and fluxes in the laboratory must necessarily be much higher than those in the ISM. We recognize that the morphology of the sample could make a difference in the processes here investigated, since we expect the sticking coefficient to be higher for a crystalline rather than an amorphous structure, while the atom mobility should be lower.

In this paper we present a set of results on the measured hydrogen recombination efficiency as a function of sample temperature and on the kinetics of the processes involved. Such results can shed new light on the problem of H recombination on interstellar grains.

2. Experimental

The apparatus has been described previously (Pirronello et al. 1997); here we recall a few essential features. The measurements were carried out in a ultra-high vacuum (UHV) stainless steel chamber with operating pressure in the $10^{-10} \sim 10^{-9}$ torr range. The sample is placed on a copper holder that is attached to a cold finger. The sample temperature, measured by two thermocouples, can be lowered to 5 K by circulating liquid He. The sample, a natural slab of olivine mechanically polished and with a shiny appearance, is initially cleaned in a methanol bath and, once inside the UHV chamber, is heated to ~ 200 $°C$ prior to each run for further cleaning. A copper shroud surrounds the copper holder except in front where the sample is placed. Atomic hydrogen and deuterium (obtained dissociating H_2 and D_2 in two distinct water-cooled radio frequency sources) are introduced

into the chamber through two separate, triple differentially pumped lines. A quadrupole mass spectrometer is used to detect HD. This arrangement gives two advantages. First, the background at mass 3 (HD) is very low in the UHV chamber. Second, H and D atoms encounter each other for the very first time on the cold target surface and no undissociated H_2 or D_2 coming from the atomic sources could be confused with molecules synthesized on the cold silicate surface.

The following procedure was used. First, we measured the intensity of the two well collimated beams of H and D atoms entering the chamber; then, after positioning the quadrupole probe in front of the target, we measured the amount of HD coming from the surface. The HD signal was monitored both during the irradiation of the surface, I_{irr} (to detect molecules synthesized and promptly restored to the gas phase), and just after the end of irradiation, I_{des}, during a Thermal Programmed Desorption (TPD) run, in which HD desorbed during a rapid ($\sim$ 1 K/sec) heat pulse to the sample. The sum, $I_{irr} + I_{des}$, was divided by the H and D signal, I_{in}, measured on the beams entering the chamber to get what we call the recombination efficiency $r = (I_{irr} + I_{des})/I_{in}$. The values of r are corrected to take into account that, together with HD, also H_2 and D_2 molecules are synthesized; thus, r values (with $0 < r < 1$) represent the *total recombination efficiency of molecular hydrogen*, and is related to R_{H_2} (the recombination rate) by: $r = 2R_{H_2}/(n_H v_H A n_g)$.

3. Results

The large majority of atoms hitting the surface are reflected back in the gas phase, since the sticking coefficient is very low (Pirronello et al. 1997, Lin and Vidali 1996). These atoms are pumped away, except for some that form HD on the chamber walls and contribute to the increase in the background signal. Depending on their mobility, some of those that become adsorbed on the surface remain trapped in deep adsorption sites,

while others migrate and form HD. We conservatively assume that the difference between the background signal during and before irradiation is due to HD that has formed on the surface and has been promptly released in the gas phase. For this reason, this yield obtained during irradiation has to be considered an upper limit. At the lower end ($\sim 5 - 7K$) of the sample temperature range, this latter yield contributes only a few % to the signal due to HD that is formed on the surface.

In Fig. 1 we plot r (the recombination effciency) at different irradiation temperatures of the sample. For each temperature, we plot the contribution to r measured during irradiation only (triangles), the contribution coming from the thermal desorption run (empty squares), and the sum of the two contributions (filled squares).

Fig. 1 shows that the contribution to r from hydrogen stuck on the surface after irradiation decreases with temperature (since the residence time decreases with T), while the signal during irradiation increases with temperature, but the cumulative effect is to cause an overall reduction in molecular hydrogen production.

As discussed in the previous section, the recombination efficiency during irradiation is evaluated under the very conservative assumption that the signal during irradiation is to be ascribed solely to molecules coming from the sample. Furthermore, toward the higher end of the temperature range, the signal during the TPD run becomes very small, and the real desorption yield could be smaller than reported. For these reasons, we think that the overall recombination efficiency is closer to the lower curve (empty squares) than to the upper one (filled squares). In our previous paper (Pirronello et al. 1997), the recombination efficiency quoted at 10∼15 K refers to this lower estimate.

The values and trend as a function of temperature of r obtained here (see Fig.1) are intermediate between that of Hollenbach and Salpeter (Hollenbach and Salpeter 1970 and 1971), Leicht-Devlin and Williams (Leitch-Devlin and Williams 1984 and 1985) and Buch

and Zhang (Buch and Zhang 1991) on one side, and of Smoluchowski (Smoluchowski 1981 and 1983) on the other, but clearly closer to the calculated value of the first group of authors. In Hollenbach and Salpeter's model $S \sim 0.3$, $\gamma = 1$; thus, in that case r would be equal to 0.3 (temperature independent). Smoluchowski 's approach takes into account the amorphous structure of grains and employs a fully quantum mechanical approach. In that case r is several orders of magnitude lower and strongly temperature dependent. Obviously, it would be of great value to carry out experiments on amorphous samples.

To reach a better understanding of how these results apply to interstellar environments, we carefully analyzed desorption spectra. Desorption dynamics, in fact, can be related in a straightforward manner to specific microscopic processes occurring on the surface. In Fig. 2 a series of TPD runs is shown after irradiation of H and D at the lowest sample temperature and for irradiation times from 5 sec to 480 sec, where the saturation coverage is reached at around 60 min of irradiation (see Pirronello et al. 1997).

The analysis of the desorption kinetics shown in the spectra of Fig. 2 can be carried out according to the Polanyi-Wigner equation (Redhead 1962):

$$- dN(t)/dt = \nu_\alpha N(t)^\alpha exp(-E_{des}/k_B T) \tag{2}$$

where $dN(t)/dt$ is the rate of desorption, α is the so-called reaction order, ν_α is a frequency factor, $N(t)$ is number of adsorbed atoms or molecules, E_{des} is the energy barrier for desorption, k_B is the Boltzmann constant, and T is the absolute temperature.

In such a simple Arrhenius-type equation the coverage dependence is entirely contained in the N-term, the pre-exponential term represents the frequency (number of times per second) the adsorbate attempts to overcome the barrier. The exponential term represents the fraction of attempts with the required minimum energy. An inspection of Eq. (2) shows that: when $\alpha = 0$, the desorption rate is independent of coverage (such as in the case where the reaction is the desorption from a multilayer adsorbate and desorption spectra

show a common low temperature edge); when $\alpha = 1$, the desorption rate is proportional to the surface coverage (for example, when the reaction is just the desorption from one layer of already formed molecules, the peak position in desorption spectra doesn't change with coverage and peak shapes are asymmetric due to the sudden depletion of the adsorbate); when $\alpha = 2$, the desorption rate is proportional to the square of the adsorbate density (as when the reaction occurs between two adsorbed species that become mobile on the surface and react with each other before desorbing; the desorption spectra have a common high-temperature tail and the position of the maximum shifts as a function of coverage as it can be seen by taking the derivative of Eq.(2) (Chan et al. 1978).

In the bottom part of the Fig. 2, at the lowest coverage the desorption kinetics is clearly of the second order. Using this analysis for the curves at the bottom of Fig.2, we get the desorption energy within ± 0.1 meV. Due to uncertainty in the saturation coverage, we quote $E_{des} = 25.5 \pm 0.6$ meV.

At intermediate coverage, desorption curves have a much reduced shift in the peak positions but they are still symmetric (see Fig. 2 in Pirronello et al. 1997). At higher coverages, but below monolayer coverage, peak shapes have characteristics of first order desorption kinetics (top part of Fig. 2), which is typically characterized by the same peak position (for increasing coverage) with a strong asymmetry between the low vs. high temperature sides.

4.   Discussion

Our set of experiments, carried out at temperatures of 5~7 K and up, gives convincing evidence of the fact that the formation of molecular hydrogen on a surface is a thermally activated process characterized by the existence of a threshold temperature that will likely

depend on the nature (i.e, chemical composition and structure) of the grain surface.

The fact that in the low coverage regime the desorption is of the second order means that at low surface temperature atoms accomodate on the surface and remain localized as atoms without recombining. If they recombined, desorption would be of the first order. In turn, this implies that tunneling at low temperature is not sufficient by itself to assure the mobility of hydrogen adatoms. Such mobility is required for hydrogen atoms in order to scan all the adsorption sites on the grain and encounter each other, according to the model of Hollenbach and Salpeter.

According to the experimental evidence on desorption kinetics, and in agreement with the analysis of peaks performed according to Eq.(2), we propose that, in interstellar clouds, whenever the temperature of grains is such as to maintain a low coverage regime, the appropriate expression for the production rate $R_{H_2}(cm^{-3}sec^{-1})$ of molecular hydrogen , should be:

$$R_{H_2} = \frac{1}{2}(S_H n_H v_H A t_H)^2 n_g \tilde{N}^{-2} \nu f(T, a, \delta E)\gamma\prime, \tag{3}$$

The term squared in Eq. (3) represents the total number of H atoms on the grain surface and the $\tilde{N}^{-2}\nu f(T, a, \delta E)$ describes the mobility of adatoms due both to thermal activation and tunneling, two processes that can be in competition with or help each other. The cross-sectional area A can be written as $N^{2/D}\sigma$, where N is the number of sites, σ the area of each adsorption site, and D is the fractal dimension (likely to be from 2 to ~ 2.6 for many non-porous carbon and silicon-bearing solids; see, Avnir et al. 1984); $t_H = \nu_H^{-1}exp(D_H/k_B T)$ is the residence time of H atoms (ν_H is a characteristic frequency of an H atom in the energy level D_H inside the adsorption potential well), $\tilde{N}$ is the average number of sites between two adsorbed H atoms ($\tilde{N}$ is squared to take into account that adatoms perform random walks), ν an inverse characteristic time related to atom diffusion, T is the temperature, δE and a are energy and width parameters for tunneling. The

function f might be obtained, in analogy to electric conduction in non-crystalline materials, by the "variable range hopping" theory: $f = f_0 \, exp(-B/k_B T^{1/3})$ (Mott 1987). $\gamma\prime$ is the probability that two H adatoms recombine upon encountering.

An additional process to be considered in interstellar environments is the competition between H atoms and already formed H_2 molecules (coming from the gas phase) to occupy the available adsorption sites on the grain. In this case, the number of available adsorption sites on the grain is $(1 - S_{H_2} n_{H_2} v_{H_2} N \sigma t_{H_2})$.

The top panel of Fig.2 shows that at higher coverage, but still lower than one layer, the shape of the desorption peaks assume the characteristics of first order desorption. The straightforward interpretation is that when the coverage is high enough (close to one monolayer of H adatoms), molecular hydrogen that is formed at low temperature doesn't leave the surface until the temperature is raised. By the way, accepting this scenario implies that, in astrophysical environments, the release of 4.5 eV in the recombination reaction doesn't necessarily restore promptly H_2 in the gas phase. Another possible interpretation is that adsorbed H atoms are so close to each other that, when mobility is increased by raising the temperature, a high fraction of them recombine and are released in the gas phase with a second order desorption kinetics that is so fast that it mimics a first order one.

In this coverage range, the rate limiting process is not diffusion because H atoms are separated by short distances, and in agreement with the first order desorption kinetics observed in our experiments, and in agreement with Eq.(2), the appropriate way to calculate the H_2 production rate $R_{H_2}(cm^{-3}sec^{-1})$ in clouds is given by the expression linear in N(t):

$$R_{H2} = \frac{1}{2}(S_H v_H n_H A t_H) n_g \nu f(T, a, \delta) \tilde{N}^{-1} \gamma\prime \qquad (4)$$

where the term $\tilde{N}$ doesn't appear squared as in Eq.(2) because H atoms don't have enough room for a random walk.

The results of Fig. 1, show a decline with T of a $\sim$ factor ten from 5 K to 15 K. This cannot be described by Eq.(1) (no T dependence), nor Eqs.(3) and (4) (far steeper T dependence with $\gamma\prime = 1$). We suggest that $\gamma\prime$ (Eqs. (3) and (4)) might be different from 1 and temperature dependent. This could be the case if there is a small activation barrier $E_{\gamma\prime}$ for recombination. Take $D_H \sim 15$ meV (obtained by assuming that $D_H/D_{H_2} \sim \frac{3}{4}$ is the same for olivine and graphite and that the desorption energy $E_{des} \sim$ adsorption energy); then the temperature dependence of r in Fig. 1 is reproduced with $E_{\gamma\prime} \sim 18$ meV and ~ 5 meV if Eq.(3) and (4) are used, respectively (We assumed a barrier for diffusion $\sim 0.3 \ D_H$ and have taken the usual corrections for isotopes).

Several could be the implications of these results for both the astrochemistry and general understanding of the dust component of interstellar clouds. For instance, as a consequence of the increase of the exposed grain surface (see Pirronello et al. 1997), due to the necessity to reconcile our experimental data with astronomical observations (Jura 1975), rates of other surface reactions will have to be evaluated to reassess their importance at the light of the increased surface area of the grain. Such an increment in the area will be probably due to an amorphous or porous structure of the grain, whose surface will be characterized by a high degree of roughness, the presence of voids, etc. As a major consequence, optical properties of grains could be significantly affected.

Certainly more experimental effort in the study of reaction rates on amorphous surfaces is necessary to further clarify the implications of these measurements.

REFERENCES

Avnir, D., Farin, D., and Pfeifer, P. 1984, Nature 308, 261.

Brackmann, R.T. and Fite, W.L. 1961, J.Chem.Phys. 34, 1572.

Buch, V. and Zhang, Q. 1991, Astrophys. J. 379, 647.

Chan, C.M., Aris, R., and Weinberg, W.H. 1978, Appl.Surf.Sci. 1, 360.

Draine, B.T. and Lee, H.M. 1984, Astophys. J. 285, 89.

Duley, W.W. and Williams, D.A. 1986, M.N.R.A.S. 223, 177.

Gould, R.J. and Salpeter, E.E. 1963 Astrophys.J. 138, 393.

Greenberg, J.M., and Li, A. 1996, Astron.Astrophys. 309, 258, and references cited therein.

Hong, S.S. and Greenberg, J.M. 1980, Astron.Astrophys. 88, 194.

Hollenbach, D. and Salpeter, E.E., 1970, J. Chem Phys. 53, 79; 1971, Astrophys. J. 163, 155.

Jura, M. 1975, Astrophys.J. 197, 575.

Leitch-Devlin, M.A. and Williams, D.A. 1984, M.N.R.A.S. 210, 577; 1985, ibidem 213, 295.

Lin, J. and Vidali, G. 1996, in "The Cosmic Dust Connection", Ed. by M.Greenberg, (Kluwer Academic Press) p. 323.

Mathis, J.S. and Whiffen, G. 1989, Astrophys.J. 341, 808.

Mott,N. 1987, in "Conduction in Non-Crystalline Materials"(Clarendon Press, Oxford) p. 27.

Pirronello, V., Liu, C., Shen L., and Vidali, G. 1997, Astrophys.J. 475, L69.

Redhead, P.A. 1962 Vacuum 12, 203.

Rendulic, K.D. 1992, Surf. Science 272, 34.

Schutte, A., Bassi, D., Tommasini, F., Turelli, F., Scoles, G., Herman, L.J.F. 1976, J.Chem.Phys. 64, 4135.

Smoluchowski, R. 1981, Astrophys. Space Sci. 75, 353; 1983, J. Phys. Chem. 87, 4229.

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Fig. 1.— Recombination efficiency r of hydrogen on an olivine slab as a function of temperature: computed during irradiation time (triangles), from the thermal desorption run (empty squares), and sum of the two contributions above (filled squares). Irradiation time: $\sim 1min$. Lines are guides to the eye.

Fig. 2.— Desorption rate of HD during thermal desorption runs from an olivine slab at T$\sim$ 6 K. Bottom panel: after irradiation for (bottom to top) 0.07, 0.10, 0.25, 0.55 minutes; top panel: after irradiation for (bottom to top) 2.0, 5.5 and 8.0 minutes.